

ADVANCED INORGANIC CHEMISTRY

A Comprehensive Text

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APPENDIX C

Other Nitrogen Heterocycles²⁸

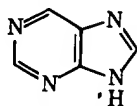
In addition to bipyridine and related heterocycles, there are numerous other heterocycles that give uni- or multidentate complexes. Some of the more important are:



Pyridazine



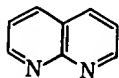
Pyrimidine



Purine



Pyrazine



1,8-Naphthyridine



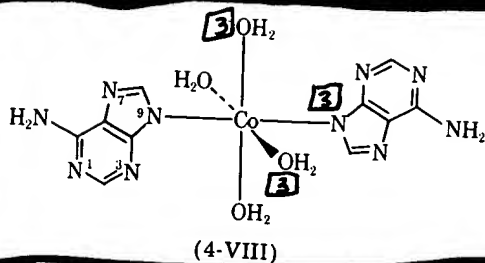
Pyrazolate



Imidazolate

One of the most important areas of concern for metal binding with nucleotides, purines, and pyrimidines arises because of their presence in nucleic acids.²⁹ The use of certain metal complexes, notably *cis*-PtCl₂(NH₃)₂, as anticancer agents, is believed to arise through binding to nucleic acids. Other aspects of the binding of metal complexes to nucleic acids include the attachment of lanthanide ions as shift reagents for fluorescent probes and the use of heavy metals to assist in X-ray structural determinations.

For unsubstituted purines, the most likely binding site for coordination is the N9 position (N-9), which is protonated in the free neutral ligand. An example is the complex of adenine, [Co(ad)₂(H₂O)₂]⁺ (4-VIII).

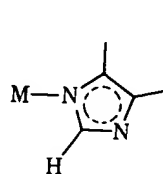


(4-VIII)

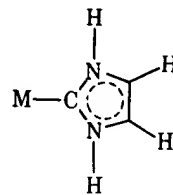
See also M. Kubo, *Coord. Chem. Rev.* 1976, 21, 1; B. C. Bunker et al., *J. Chem. Soc., Dalton Trans.*, 1978, 17, 173; W. L. Hatfield, *J.C.S. Dalton*, 1978, 868 (pyridazine, pyrazine); J. G. Vos and J. Groenvelt, *Inorg. Chim. Acta*, 1978, 27, 173 (pyrazolate); Fischer and R. Bau, *Inorg. Chem.*, 1978, 17, 27; D. J. Hodgson, *Prog. Inorg. Chem.*, 1977, 11 (stereochemistry of complexes); L. G. Marzilli, *Prog. Inorg. Chem.*, 1977, 23, 256 (metal interactions); L. G. Marzilli and T. J. Kistenmacher, *Acc. Chem. Res.*, 1977, 10, 146; G. Matikakis et al., *Inorg. Chem.*, 1978, 17, 915 (Pd^{II}).

If the 9-position is blocked, the other imidazole nitrogen, N-7, is coordinated. Binding appears somewhat less likely through N-1 than through N-7; three complexes established by X-ray crystallography, two also involving both N-1 and N-7.

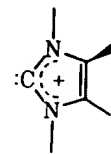
Imidazoles^{30a} have been widely studied. Although the binding is usually to the N atom (4-IX), in some Ru^{II}, Ru^{III}, Fe⁰, and Cr⁰ complexes it is possible to have C-bonded groups^{30b} (4-X).



(4-IX)



(4-X)

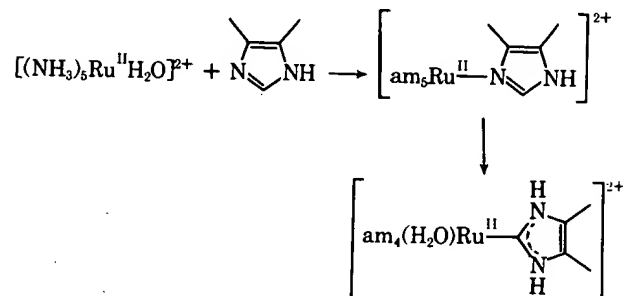


(4-XI)

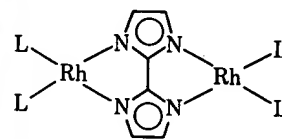
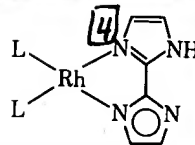


(4-XII)

The C-bonded entity can be regarded as a carbene (4-XI) (see Chapter 4) or as a C-bound amidine³¹ (4-XII). An example of a C-bonded species is the Ru(II) complex obtained as follows:



The N-bonded imidazoles commonly form bridges between two metal centers as in $[\text{Cu}_3(\text{imH})_6(\text{im})_3]^{4+}$ and $[\text{Co}(\text{im})(\text{TPP})\text{THF}]_n$, where TPP is tetraphenylporphyrin. Bimidazoles can act as mono or dianions,³³ for example, sodium(1) and sodium(2) complexes.



^{30a} R. J. Sunderburg and R. B. Martin, *Chem. Rev.*, 1974, **74**, 471 (imidazole and histidine complexes).

^{30b} R. J. Sunderburg *et al.*, *J. Am. Chem. Soc.*, 1974, **96**, 381; *Inorg. Chem.*, 1977, **16**, 1515; and H. Taube, *Inorg. Chem.*, 1976, **15**, 3070.

³¹ D. J. Doonan, J. E. Parks, and A. L. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 2129.

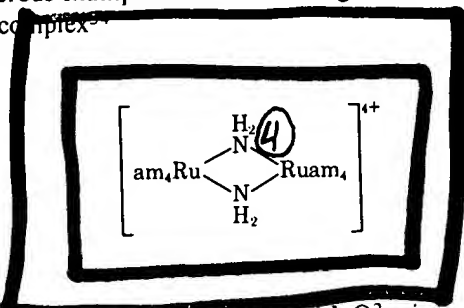
³² G. Kolks *et al.*, *J. Am. Chem. Soc.*, 1976, **98**, 5720; J. T. Landrum *et al.*, *J. Am. Chem. Soc.*, 1976, **98**, 3232; M. S. Haddad *et al.*, *Inorg. Chem.*, 1979, **18**, 141.

³³ S. W. Kaiser *et al.*, *Inorg. Chem.*, 1976, **15**, 2681.

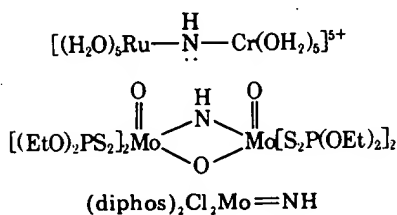
4-12: Ligands Derived by Deprotonation of Ammonia and Amines: Alkylamido, Nitrene, and Nitrido Complexes

Ammonia can be deprotonated by alkali metals to give the anions NH_2^- , NH^{2-} , and N^{3-} , and all of these species can act as ligands.

There are numerous examples of the *amido* ligand NH_2 acting as a bridge, as in the ruthenium complex³⁴



The imido ion NH^- , which is isoelectronic with O^{2-} , is not common as a ligand, although its alkyl and aryl derivatives NR are (see below). Some examples³⁵ of complexes, which have terminal or bent bridged NH groups, are the following species:



Nitrido Complexes have N^{3-} bound in the following ways:

Multiply Bonded Nitride $\text{M}\equiv\text{N}$.³⁶ Here the nitride ion is forming three covalent bonds to the metal; it is one of the strongest π donors known. The compounds are rather similar to those containing $\text{M}=\text{O}$ groups (Section 4-23). The complexes are largely those of molybdenum, tungsten, rhenium, ruthenium, and osmium, examples being $\text{NReCl}_2(\text{PPh}_3)_2$, $[\text{NOsCl}_5]^{2-}$, and $[\text{NOsO}_3]^-$. The $\text{M}\equiv\text{N}$ bonds are very short (ca. 1.16 Å) and the $\text{M}-\text{N}$ stretching frequencies are in the region 950–1180 cm^{-1} .

N-Bridged Species. These are of the following types:

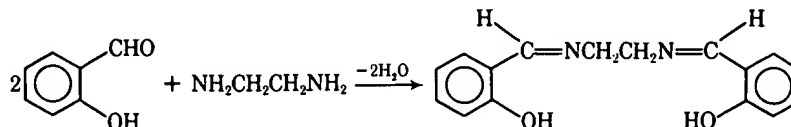
M. T. Flood et al., *Inorg. Chem.*, 1973, 12, 2153.

R. P. Cheney and J. N. Armor, *Inorg. Chem.*, 1977, 16, 3338; A. W. Edelblut, B. L. Haymore,

and R. A. D. Wentworth, *J. Am. Chem. Soc.*, 1978, 100, 2250.

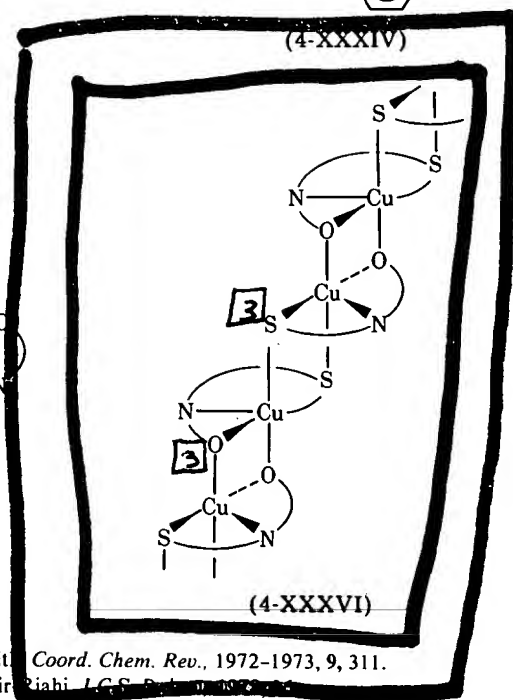
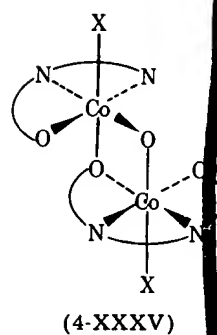
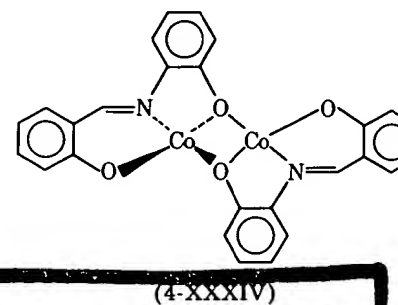
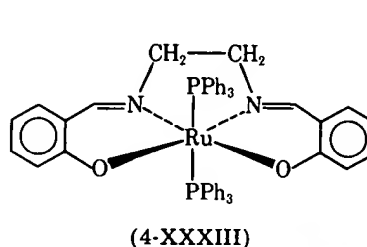
W. P. Griffith, *Coord. Chem. Rev.*, 1972, 8, 369. D. Pawson and W. P. Griffith, *J.C.S. Dalton*, 1975, 417; C. D. Cowman et al., *Inorg. Chem.*, 1976, 15, 1747.

One of the best known Schiff base ligands is bis(salicylaldehyde)ethyleneimine⁸⁸ (sal₂en):



This is a bifunctional (two OH groups), tetradentate (2N, 2O) ligand. Other Schiff bases can be mono-, di-, or tetrafunctional and can have denticities of 6 or with various donor atom combinations (e.g., for quinquedentate, N₃O₂; N₂O₂P; N₂O₂S, etc.). Complexes of un-ionized or partly ionized Schiff bases are also known⁸⁹ (e.g., LaCl₃sal₂enH₂O·aq).

Some representative types of complex that illustrate not only the formation of mononuclear but of binuclear and polymeric species are 4-XXXIII, 4-XXXIV, 4-XXXV, and 4-XXXVI.



⁸⁸ M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 1972-1973, 9, 311.

⁸⁹ J. I. Bullock and H.-A. Tajmir-Riahi, *J. Chem. Soc. Dalton Trans.*, 1972, 1022.

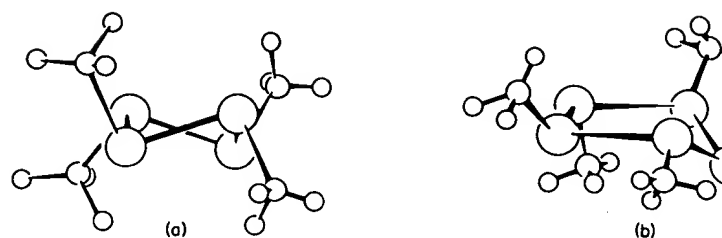
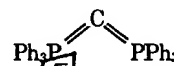


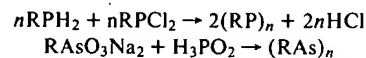
Fig. 14-11. The structures of (a) $(\text{CF}_3\text{P})_4$ and (b) $(\text{CF}_3\text{P})_5$. Large, medium, and small circles represent P, C, and F atoms, respectively.

proper must be linear ($\text{R}-\text{C}\equiv\text{C}-\text{CR}_2$), there is d -orbital participation in phosphorus compounds, which are bent.⁶⁷

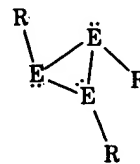


Cyclopolyphosphines and -arsines.⁶⁸ These are compounds of general formula $(\text{RP})_n$ and $(\text{RAs})_n$, $n = 3$ to 6. $(\text{C}_2\text{F}_5\text{P})_3$ is best known for $n = 3$ and $(\text{PhAs})_6$, and the three isomers $[(\text{MeC}_6\text{H}_4)\text{As}]_6$ for $n = 6$. The four-membered rings predominate, with four-membered ones being favored by substituents. The puckered structures adopted by these rings are illustrated in representative compounds in Fig. 14-11.

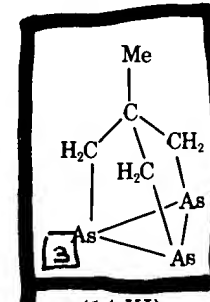
These compounds in general are thermally stable, though often react. Preparative reactions are:



The preferred conformation⁶⁹ for R_3E_3 is 14-X, but as might be expected, the chair arrangement is enforced in 14-XI.⁷⁰



(14-X)



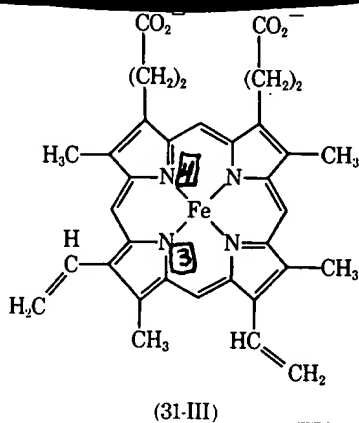
(14-XI)

⁶⁷ P. J. Carroll and D. D. Titus, *J. C. S. Dalton*, 1977, 824.

⁶⁸ L. R. Smith and J. R. Mills, *J. Organomet. Chem.*, 1975, 84, 1; *J. Am. Chem. Soc.*, 1975, 97, 3852.

⁶⁹ M. Baudler et al., *Z. Naturforsch.*, 1976, 31b, 1305, 1311.

⁷⁰ J. Ellermann and H. Schossner, *Angew. Chem., Int. Ed.*, 1974, 13, 601.

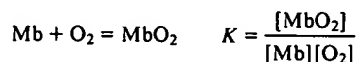


00, consists of four myoglobinlike subunits; these four are similar but not all identical, two being α units and the other β units. Neither the α nor the β units of hemoglobin have amino acid sequences that match the sequence in myoglobin, but nevertheless the ways in which the chains are coiled to give three-dimensional structures (tertiary structure) are quite similar. In each subunit of hemoglobin and myoglobin, the iron atom is also bonded to the nitrogen atom from the imidazole chain of a histidine residue. Figure 31-4 gives a schematic representation of β -subunit of hemoglobin; its essential features are typical of α -subunits and myoglobin as well.

According to the description above, the iron atoms in Hb and Mb when no oxygen is present (the deoxy forms) would be five-coordinate. In fact, there is probably a water molecule loosely bonded in the sixth position (i.e., trans to the histidine nitrogen atom) to complete a distorted octahedron. The iron atom appears to be out of the porphyrin plane toward the histidine. In both deoxy-Mb and deoxy-Hb, iron atoms are high-spin Fe^{II} , with four unpaired electrons.

The function of both Hb and Mb is to bind oxygen, but their physiological roles are very different. Hb picks up oxygen in the lungs and carries it to tissues via the circulatory system. Cellular oxygen is bound by myoglobin molecules that store it until it is required for metabolic action, whereupon they release it to other cells. Hb has an additional function, however, and that is to carry CO_2 back to the lungs; this is done by certain amino acid side chains, and the heme groups are directly involved. Because the circumstances under which Hb and Mb are required to bind and release O_2 are very different, the two substances have quite different binding constants as a function of O_2 partial pressure (Fig. 31-5).

Myoglobin is not simply a passive carrier of oxygen but an intricate molecular machine. This may be appreciated by comparing its affinity for O_2 to that of hemoglobin. For myoglobin (Mb) we have the following simple equilibrium:



where \bar{y} represents the fraction of myoglobin molecules bearing oxygen and P represents

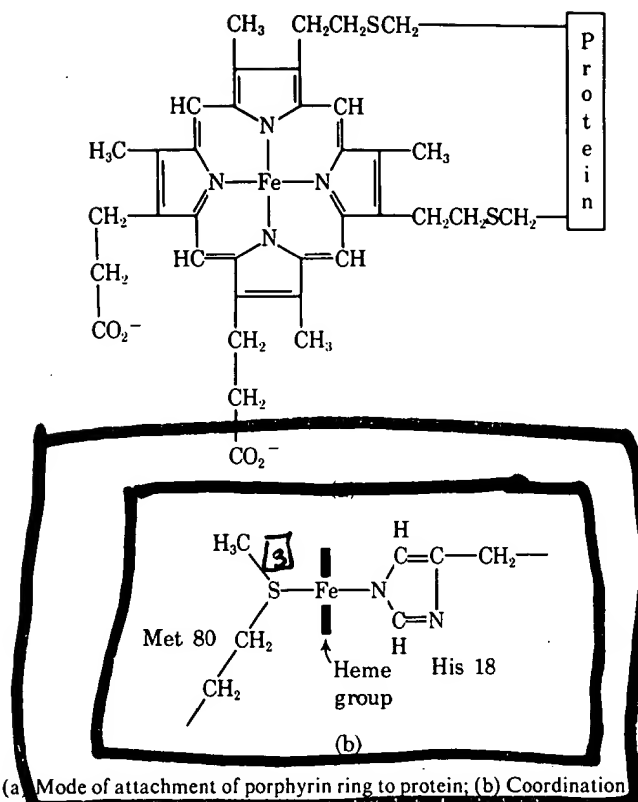


Fig. 31-8. (a) Mode of attachment of porphyrin ring to protein; (b) Coordination of the iron atom in cytochrome *c*.

tunnelling through the protein, by an outer-sphere mechanism. The folding of the protein chain is such that aside from the methionine and histidine residues that coordinate to the iron atom, the side chains that lie inside facing the heme group are the hydrophobic ones. The polar or charged side chains lie on the outside and are arranged in a unique pattern that seems to be designed to allow appropriate matching with both Cyt *c*₁ from which an electron must be accepted and cytochrome oxidase to which an electron must be transferred.

Cytochrome *c* seems to be one of the most ancient of biomolecules, having evolved in essentially its present form more than 1.5 billion years ago, even though it is present in all animals and plants, including those that have appeared more recently. It has been found that the cytochrome *c* of any eucaryotic species (one having cells with nuclei) will react with the cytochrome oxidase of any other species, thus confirming that this electron transfer chain has resisted evolutionary change for a very long time.

Cytochrome P₄₅₀ Enzymes. These heme proteins, found in cell membranes, catalyze the hydroxylation of C—H bonds; the name given to them is thus misleading, since they do not serve the type of electron transfer function just discussed for the "regular" cytochromes, but are actually enzymes. They consist of one heme

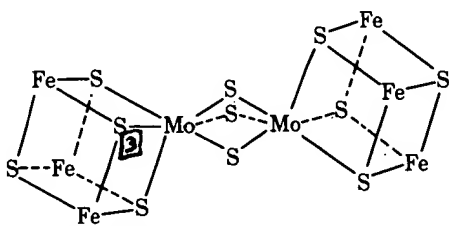


Fig. 31-17. A schematic drawing of the type of Mo-Fe-S clusters in models for the Fe-Mo-Co of nitrogenase.

established their structures by X-ray crystallography.^{45,46} The essential features of these structures are shown in Fig. 31-17. There is an RS^- ligand attached to each of the six iron atoms, as in the $Fe_4S_4(SR)_4$ systems. Perhaps the most remarkable and important observation⁴⁵ concerning these model systems is that one of them shows an Mo EXAFS pattern that is essentially superimposable on that for the Mo-co.

-11. Miscellaneous Other Metals

The Alkaline Earths. Only magnesium and calcium have biological roles; the other alkaline earths are more or less toxic.

Magnesium has several important biochemical functions. Its presence in chlorophyll, and the structure and photosynthetic activity of chlorophyll, have been mentioned (p. 284). Animal organisms also require magnesium. For example, an adult human body normally contains about 20 g, of which about half is found in the bones and the other half within cells. The major role of intracellular magnesium is to act as a cofactor for various enzymes that catalyze the hydrolysis or cleavage of polyphosphates. Among these are alkaline phosphatase (which is a zinc metal-enzyme as mentioned earlier), ATPase, hexokinase, and one or more of the deoxyribonucleases. The Mg^{2+} ion functions as a Lewis acid, polarizing the phosphate groups, thereby enhancing the possibility of nucleophilic attack on a terminal phosphorus atom.

Calcium is found almost entirely (ca. 98%) in the bones, but it has several other roles as well. It is intimately involved in the process of muscle contraction, in neuronal activity, and in at least one part of the visual process. Calcium is also believed to be an integral part of biological membranes. Several enzymes (e.g., α -amylase and thermolysin) use Ca^{2+} ions in support of their structures, and in at least one case, micrococcal nuclease, the Ca^{2+} ion has been shown to participate directly in the active site, where it is coordinated by an octahedral set of oxygen atoms.⁴⁷

There are several proteins whose function appears to be calcium storage and transport, especially in conjunction with its role in muscle contraction. The best

R. H. Holm *et al.*, *J. Am. Chem. Soc.*, 1978, 100, 4630.

C. D. Garner *et al.*, *J.C.S. Chem. Comm.*, 1978, 740.

F. A. Cotton and E. E. Hazen, Jr., *Proc. Nat. Acad. Sci. (U.S.)*, 1979, 76, 2551.